



Review

# Tetrahydroborates: Development and Potential as Hydrogen Storage Medium

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**Abstract:** The use of fossil fuels as an energy supply becomes increasingly problematic from the point of view of both environmental emissions and energy sustainability. As an alternative, hydrogen is widely regarded as a key element for a potential energy solution. However, differently from fossil fuels such as oil, gas, and coal, the production of hydrogen requires energy. Alternative and intermittent renewable energy sources such as solar power, wind power, etc., present multiple advantages for the production of hydrogen. On the one hand, the renewable sources contribute to a remarkable reduction of pollutants released to the air and on the other hand, they significantly enhance the sustainability of energy supply. In addition, the storage of energy in form of hydrogen has a huge potential to balance an effective and synergetic utilization of renewable energy sources. In this regard, hydrogen storage technology is a key technology towards the practical application of hydrogen as “energy carrier”. Among the methods available to store hydrogen, solid-state storage is the most attractive alternative from both the safety and the volumetric energy density points of view. Because of their appealing hydrogen content, complex hydrides and complex hydride-based systems have attracted considerable attention as potential energy vectors for mobile and stationary applications. In this review, the progresses made over the last century on the synthesis and development of tetrahydroborates and tetrahydroborate-based systems for hydrogen storage purposes are summarized.

**Keywords:** Tetrahydroborates; synthesis; decomposition pathways; solid state hydrogen storage

## 1. Introduction

Since the second industrial revolution in the late 19th century, humankind has experienced an uninterrupted period of industrial and economic growth. The possibility to produce energy using the so far cheap and abundant fossil fuels has represented, beyond doubt, the driving force of this growth period. All of the current energy systems are based on coal, oil, natural gas, as well as nuclear fission, depending on the conditions in a given country and its access to the cheapest primary energy source. The total final consumption of energy worldwide grew more than twice from the 1970s to

the 2000s. Unless an alternative to the use of fossil fuels is found, this trend is going to come soon to an end [1]. Moreover, the massive use of fossil fuels has disturbed the equilibrium of the global climate. The transition from a carbon-based economy to a carbon-free economy is perhaps the greatest challenge of the 21st century. Possible candidates to replace the fossil fuels as energy sources are the so called renewable energy sources (e.g., solar-, wind-, geothermal-, wave-, hydroelectric-energy, etc.). However, the main obstacle to the use of these energy sources is the fact that they are intermittent and un-evenly distributed. To fully exploit these energy sources, an efficient energy storage system is required. In this regard, hydrogen is widely considered to be capable of solving both the issues of increasing CO<sub>2</sub> emissions and of future energy sustainability. Hydrogen has a gravimetric energy density of 120 MJ/kg, which is more than twice the energy content of most common fossil fuels (e.g., methane 50 MJ/kg, propane 46 MJ/kg and gasoline 45 MJ/kg). Unfortunately, compared to fossil fuels, hydrogen, being the lightest element of the periodic table, has an extremely low volumetric energy density.

Hydrogen is usually stored in three main forms: as highly pressurized gas under 350 and 700 bar, in liquefied form at −253 °C, and in metal hydrides, chemically bonded to metals. Although, the volumetric energy density improves when hydrogen is compressed and/or liquefied, it still remains low as compared to that of fossil fuels. A significant improvement of the volumetric energy density is achieved when hydrogen is bonded to another element in solid state form [2–5]. It is well known that several metals, and in particular transition metals, have a high affinity for hydrogen. This high affinity leads to the reaction between hydrogen (H<sub>2</sub>) and the metal (M) to form metal hydrides (MH<sub>x</sub>). This process can be described as follows:



Metal hydrides such as those of Mg [6–13] and Pd [14–18] have been exhaustively studied for decades. Mg has a relative high gravimetric hydrogen density of 7.6 wt %, it is abundant, and it is cheap [12,13], however, the Mg/MgH<sub>2</sub> system presents a high thermodynamic stability ( $\Delta H_{\text{dehydrogenation}} = -74$  kJ/mol H<sub>2</sub>) [6], leading to operative temperatures above 300 °C. Thus, the thermal management for large scale use of MgH<sub>2</sub> becomes an important issue, constraining the practical applications of MgH<sub>2</sub> to the stationary ones. In the case of Pd, the absorption of hydrogen already occurs at room temperature and presents excellent catalytic properties for the dissociation of the hydrogen molecule. However, its gravimetric hydrogen density is extremely low (~0.6 wt %) and it is quite costly. Therefore, Pd is not suitable for any large scale hydrogen storage application.

Other examples of hydrides with high gravimetric hydrogen capacity but improper enthalpy of formation are aluminum hydride (AlH<sub>3</sub>, gravimetric hydrogen capacity of ~10.0 wt %), and lithium hydride (LiH, gravimetric hydrogen capacity of ~12.6 wt %). The low formation enthalpy of AlH<sub>3</sub> (5–8 kJ/mol H<sub>2</sub>) requires extreme pressure conditions for the hydrogenation of Al [19]. On the contrary, the high formation enthalpy of LiH (140 kJ/mol H<sub>2</sub>) leads to a harsh dehydrogenation temperature above 700 °C at 1 bar of hydrogen [4]. Therefore, tailoring the metal hydrides reaction enthalpies and/or developing hydrogen containing materials that are different from the conventional metal hydrides are key issues for the design of vessels based on solid-state hydrogen storage materials towards practical applications. Recently, because of their high hydrogen storage capacity, “complex hydrides” attracted considerable attention as potential hydrogen storage materials [20–23]. The name “complex hydrides” originates from the presence of an anionic non metal–hydrogen complex ([BH<sub>4</sub>]<sup>−</sup>, [NH<sub>2</sub>]<sup>−</sup>, [AlH<sub>4</sub>]<sup>−</sup>) or metal–hydrogen complex ([NiH<sub>4</sub>]<sup>4−</sup>, [CoH<sub>5</sub>]<sup>4−</sup>, [FeH<sub>6</sub>]<sup>4−</sup>, [MnH<sub>6</sub>]<sup>5−</sup>, and [ZnH<sub>4</sub>]<sup>2−</sup>) bonded to a cationic alkali, alkali-earth, or transition metal. Taking into account this formulation, the complex metal hydrides are classified as non-transition metal complex hydrides (such as LiBH<sub>4</sub>, LiNH<sub>2</sub>, LiAlH<sub>4</sub>) and transition metal complex hydrides (such as Mg<sub>2</sub>NiH<sub>4</sub>, Mg<sub>2</sub>CoH<sub>5</sub>, Mg<sub>2</sub>FeH<sub>6</sub>, Mg<sub>3</sub>MnH<sub>7</sub>, K<sub>2</sub>ZnH<sub>4</sub>). Although this class of hydrides has been known for a long time since the first report on pure metal amides was published in the 1809 [24,25], they had initially not been considered as potential hydrogen storage materials. In the case of the non-transition metal complex

hydrides, this lack of initial interest can be traced to their apparent irreversibility and more in general to the difficulty to produce them in a large scale. The interest on hydrogen as an energy carrier began around the 1960s, and it has grown significantly since the 1990s. In 1997, Bogdanovič and Schwickardi were the first to demonstrate the concrete possibility to reversibly store hydrogen in titanium-based doped NaAlH<sub>4</sub> at moderate temperature and pressure conditions [26]. Since then, many efforts have been done to investigate and optimize the hydrogen storage properties of complex hydrides.

There are several review works about light complex hydrides in which different aspects of tetrahydroborates are described [20–37]. In some works the synthesis, structure, stability, kinetics, thermodynamics, as well as tailoring of the tetrahydroborates and their hydride mixtures are covered [20–31]. Others focus on the synthesis of tetrahydroborates, high metal boranes and rare-earth borohydrides [28,32–34]. There is a review that describes the hydrogen storage properties of NaBH<sub>4</sub> [35]. In addition, some review works are mainly devoted to the crystal structures of tetrahydroborates [28,36,37].

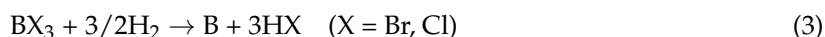
The aim of this work is to highlight selected aspects of tetrahydroborates, such as (1) a historical overview about their synthesis; (2) the different decompositions mechanisms; and (3) the conceptual background of alternative approaches to tailor their hydrogen storage properties, mainly the concept of the reactive hydride composites (RHC), along with the most relevant achievement in their use as hydrogen storage materials and future prospects.

## 2. From Boron to Tetrahydroborates

In the last two centuries, boron has gained a significant importance in our daily life. This low-abundance element and its compounds are used in a variety of branches, including agriculture, medicine, electronics, chemical synthesis, catalysis, and energy. Highly impure boron was isolated for the first time in 1808 by H. Davy [38] J. L. Gay Lussac and L. J. Thénard [39]. In 1892 H. Moissan obtained boron with a purity of roughly 95% by the reduction of borax with magnesium, as shown in reaction (2) [40]:

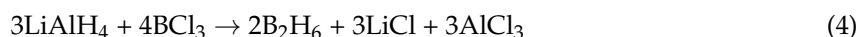


However, high-purity boron (>99.9%) was isolated only in 1922 when a new synthetic pathway that was capable to ensure a kilograms scale production was introduced. In that process volatile boron compounds (i.e., BBr<sub>3</sub> and BCl<sub>3</sub>) were reduced by H<sub>2</sub> at temperatures between 800 °C and 1200 °C (reaction (3)). The temperature of the process was selective for the final boron allotrope [41].



Together with the availability of good purity boron, the preparation and characterization of boron hydrides started in 1912. Thanks to the work of A. Stock and co-workers in the period between the 1912 and 1936, six boron hydrides, i.e., B<sub>2</sub>H<sub>6</sub>, B<sub>4</sub>H<sub>10</sub>, B<sub>5</sub>H<sub>9</sub>, B<sub>5</sub>H<sub>11</sub>, B<sub>6</sub>H<sub>10</sub>, and B<sub>10</sub>H<sub>14</sub>, were isolated and their chemical features investigated [42–44]. The early syntheses of boron hydrides were based upon the reaction between magnesium boride and hydrochloric acid. This preparation pathway was largely inefficient often giving mixtures of products (B<sub>y</sub>H<sub>x</sub>, y = 4, 5, 6, 10, x = 9, 10, 14), with yields of only 4–5% [44]. A first improvement in the reaction yield (11%) was achieved replacing the hydrochloric acid with 8N-phosphoric acid.

At this time, diborane was obtained in millimolar quantities by the thermal decomposition of B<sub>4</sub>H<sub>10</sub>, and later in the 1931 H. Schlesinger and A. B. Burg reported the synthesis of B<sub>2</sub>H<sub>6</sub> from BCl<sub>3</sub> and H<sub>2</sub>, using a high voltage discharge [45]. Despite the fact that the amount of B<sub>2</sub>H<sub>6</sub> produced by this method was still small, the reaction provided a considerable yield of 75%. It was necessary to wait until 1947 to find an effective and practical method to synthesize B<sub>2</sub>H<sub>6</sub> with a purity of 99% [46]. This method was based on a halide-hydride exchange reaction performed in ethyl ether according to reaction (4):



In the following years, several useful routes to synthesize  $B_2H_6$  via halide-hydride exchange reaction were found, as for example, the reactions between  $NaH$  with  $B(OCH_3)_3$ ,  $BH_4^-$  with  $I_2$  and  $BH_4^-$  with  $H_2PO_4$  [47–51].

Along with the increasing availability of  $B_2H_6$ , the synthesis of new compounds was enabled. The first tetrahydroborate, i.e.,  $Al(BH_4)_3$ , was produced in 1940 starting from trimethylaluminium and diborane (reaction (5) [52]):

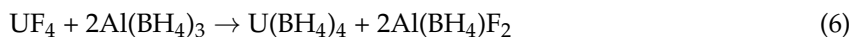


To synthesize significant quantities of tetrahydroborates and to limit the formation of complex mixtures as side-products, the reaction had to be performed in an excess of diborane. The stoichiometric formula of the aluminum tetrahydroborate was obtained by the characterization of the vapor density and the evaluation of the reaction between the newly synthesized compound with water and hydrogen chloride. The isolated material was a colorless solid below  $-64.5^\circ C$ , its vapor pressure measured at  $0^\circ C$  was 119.5 mm Hg, and its extrapolated boiling point was  $44.5^\circ C$ .

Encouraged by the close chemical similarities between aluminum and beryllium, A. B. Burg and H. I. Schlesinger [53] successfully synthesized beryllium tetrahydroborate, following the same approach as used for the synthesis of aluminum tetrahydroborate. The reaction of dimethylberyllium with diborane proceeds in several steps towards the formation of beryllium tetrahydroborate, i.e.,  $Be(BH_4)_2$ . In the first step, a solid methyl-rich compound with unknown composition is formed. Then, this compound turns into a non-volatile liquid. Upon further reaction with  $B_2H_6$ , an easily sublimable solid is produced. This solid has an approximate composition formula  $CH_3BeBH_4$ . The addition of further  $B_2H_6$  leads to the formation of beryllium tetrahydroborate coexisting with a mixture of other derivatives of diborane compounds in gas form, such as boron trimethyl and methyl plus a non-volatile beryllium hydroborate species. Due to its complexity, the synthesis of  $Be(BH_4)_2$  through this route cannot be summarized in a simple chemical equation.

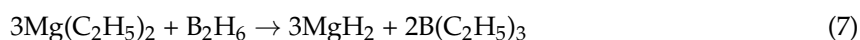
In the same year, H. I. Schlesinger and H. C. Brown [54] investigated the possibility of forming tetrahydroborates of alkali metals. Because of its simple preparation and purification routes, ethyllithium ( $LiC_2H_5$ ) was chosen as starting material. Once ethyllithium and  $B_2H_6$  were put into contact, they reacted to form several ethyl derivatives of diborane plus the solid tetrahydroborates of lithium ( $LiBH_4$ ). This compound is characterized by a rather high stability. In fact, differently from the aluminum and beryllium tetrahydroborate, that ignite spontaneously when exposed to air at room temperature,  $LiBH_4$  is quite stable in dry air.

In 1941, H. I. Schlesinger and co-workers [55] were asked to undertake the synthesis of new volatile compounds of uranium. As a consequence of the fact that the tetrahydroborates of aluminum and beryllium are the most volatile compounds of these elements, the synthesis of uranium tetrahydroborate was attempted [53,56]. Although, the tetrahydroborates of aluminum, beryllium, and lithium were prepared by the reaction of diborane with metal alkyls, no alkyl of uranium was known at that time. Therefore, a new synthetic procedure was developed. Uranium tetrahydroborate was obtained by the interaction of uranium (IV) fluoride with aluminum tetrahydroborate, as shown in reaction (6):



At the time of its first synthesis, uranium tetrahydroborate was the most volatile compound of the known uranium (IV) derivatives.

In 1950, E. Wiberg and R. Bauer were the first to synthesize  $Mg(BH_4)_2$  by the production of fine magnesium hydride powder, reaction (7), and then its subsequent reaction with diborane, reaction (8) [57]:

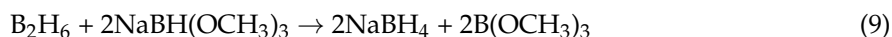


Until that year, the following tetrahydroborates were prepared by the interaction of diborane with metal derivatives:  $\text{HZn}(\text{BH}_4)$ ,  $\text{Ga}(\text{BH}_4)$ ,  $\text{Ti}(\text{BH}_4)_3$ ,  $\text{Pu}(\text{BH}_4)_3$ ,  $\text{Zr}(\text{BH}_4)_4$ ,  $\text{Hf}(\text{BH}_4)_4$ ,  $\text{Th}(\text{BH}_4)_4$ ,  $\text{Np}(\text{BH}_4)_4$  [57].

In 1952–1953, U.S. scientists were requested to synthesize larger amounts of borohydride by a more efficient method. The complexity of the process utilized for their synthesis involved slow reaction and repeated treatment with large excess of diborane. Thus, a more satisfactory synthetic method was developed for preparing lithium borohydride, and from it, sodium and potassium tetrahydroborate.

In solvent environment (ethyl ether) lithium hydride absorbs large quantities of diborane. After the filtration of the insoluble  $\text{LiH}$  impurities, the evaporation of the solvent from the filtrate leads to the precipitation of  $\text{LiBH}_4 \cdot (\text{C}_2\text{H}_5)_2\text{O}$  first, and then to high purity  $\text{LiBH}_4$ . At that time, it was believed that in the absence of solvents, lithium hydride does not react with diborane even at an elevated temperature [55]. However, recently Friedrichs et al. [58] showed that the solvent-free synthesis of  $\text{LiBH}_4$  from  $\text{LiH}$  in a diborane atmosphere at  $120^\circ\text{C}$  is possible.

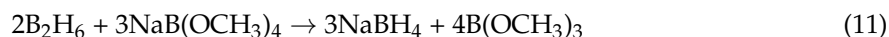
Differently from lithium hydride, sodium hydride does not react with diborane even in the presence of solvents. In order to circumvent this inconvenience the use of trimethoxyborohydride as hydride ions source was proposed [55,59]. The reaction between trimethoxyborohydride and diborane proceeds rapidly and quantitatively forming sodium tetrahydroborate and trimethylborate, according to reaction (9):



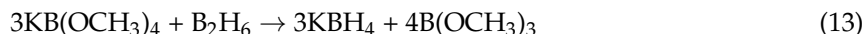
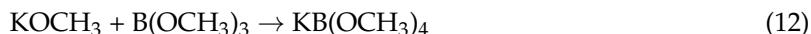
It was also reported that dimethoxiborane reacts with sodium trimethoxyborohydride to form sodium tetrahydroborate and trimethylborate as shown in reaction (10):



Similarly, diborane reacts with sodium tetramethoxyborohydride to form sodium tetrahydroborate plus trimethylborate (reaction (11)):



Following the same approach applied for the previously discussed tetrahydroborates, potassium tetrahydroborate was also synthesized for the first time by the reaction of diborane with potassium tetramethoxyborohydride (reaction (13)) [59]. The latter was synthesized from potassium methoxyde and methyl borate as shown in reaction (12):



Although, these methods allowed Schlesinger and co-workers to synthesize sodium tetrahydroborates in laboratory scale, they were not appropriate for an industrial scale production. In particular, the risks connected to the use of diborane represented a serious limitation to the scaling up the above mentioned processes. The first attempt to synthesize sodium tetrahydroborate without the use of diborane was carried out heating sodium trimethoxyborohydride to about  $230^\circ\text{C}$  [59]. At this temperature, the disproportion of the starting material to  $\text{NaBH}_4$  and  $\text{NaB}(\text{OCH}_3)_4$  takes place via reaction (14):



However, reaction (14) does not proceed to completeness at about  $230^\circ\text{C}$ . Then, the attempts to improve the yield of this reaction were stopped when in the same laboratory it was observed that sodium hydride and methyl borate quickly reacted at high temperature, i.e.,  $225\text{--}275^\circ\text{C}$ , to form  $\text{NaBH}_4$  and  $\text{NaOCH}_3$  (reaction (15)):

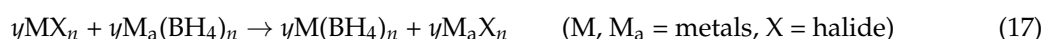




As a consequence of the extremely good yield of this reaction, i.e., 94%, and the high purity of the obtained  $\text{NaBH}_4$  up to 96%, this method is still the most used synthesis process to obtain sodium tetrahydroborate. Similarly, high purity  $\text{LiBH}_4$ , i.e., 95%, was synthesized by the reaction between lithium hydride and methyl borate with an overall reaction yield of 70% (reaction (16)):



The possibility to produce  $\text{NaBH}_4$  and  $\text{LiBH}_4$  in large quantities led to the development of a new method to successfully synthesize metal tetrahydroborates. The method consists in the metathesis between metal halides and alkali tetrahydroborates in solvents, reaction (17) [60–62]:



The first example of this reaction reported in literature was the metathesis between lithium tetrahydroborate and aluminum chloride as shown in reaction (18):



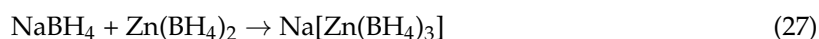
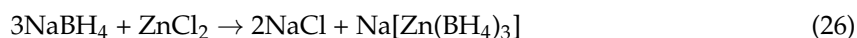
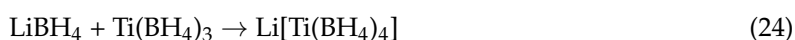
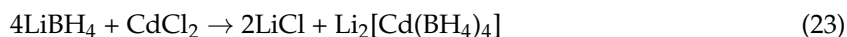
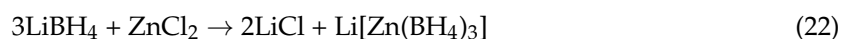
The interaction between tetrahydroborates and metal halides leads also to the formation of multi-cation tetrahydroborates. E. Wiber and W. Henle [61,62] reported on the synthesis of  $\text{Li}[\text{ZnCl}(\text{BH}_4)_2]$  and  $\text{Li}[\text{CdCl}(\text{BH}_4)_2]$  as intermediates of the syntheses of  $\text{Zn}(\text{BH}_4)_2$  and  $\text{Cd}(\text{BH}_4)_2$  via metathesis between lithium tetrahydroborate and  $\text{ZnCl}_2$  and  $\text{CdCl}_2$ , respectively, as seen in reactions (19) and (20):



In 1955, E. Wiberg and R. Hartwimmer [63] reported for the first time on the synthesis of calcium, strontium and barium tetrahydroborates, i.e.,  $\text{Ca}(\text{BH}_4)_2$ ,  $\text{Sr}(\text{BH}_4)_2$ ,  $\text{Ba}(\text{BH}_4)_2$ , respectively. The synthesis was performed by the reaction between the hydrides of the mentioned elements and diborane (reaction (21)).



In 1961, H. Nöth [64] synthesized several new multi-cation tetrahydroborates via metathesis between lithium, sodium and potassium tetrahydroborates and metal halides or by direct reaction between tetrahydroborates, i.e.,  $\text{Li}[\text{Zn}(\text{BH}_4)_3]$ ,  $\text{Li}_2[\text{Cd}(\text{BH}_4)_4]$ ,  $\text{Li}[\text{Ti}(\text{BH}_4)_4]$ ,  $\text{Li}[\text{Fe}(\text{BH}_4)_3]$ ,  $\text{Na}[\text{Zn}(\text{BH}_4)_3]$ ,  $\text{K}_2[\text{Zn}_3(\text{BH}_4)_8]$ , plus a long series of halogen derivatives as for example  $\text{Li}_2[\text{ZnI}_2(\text{BH}_4)_2]$ ,  $\text{Li}_3[\text{Mn}(\text{BH}_4)_3\text{I}_2]$ , etc. The syntheses of some of these multi-cation tetrahydroborates are described in reactions (22)–(28):

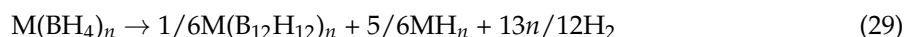


In the following years, it was possible to observe an increasing attention towards this class of materials both as laboratory reagents and as energy storage materials. As a consequence, several new tetrahydroborates were synthesized. Nowadays, the mono-cation tetrahydroborates of 32 chemical elements, plus an undefined number of multi-cation tetrahydroborates are known [23,38,42–45,52–57,59–78].

The development of the borane chemistry in general, and of the tetrahydroborates in particular, was from the early beginning connected with the research in the field of energy storage. In fact, the research in this field was stirred by the need of finding new propellants for military applications by the U.S. and Soviet Union [79]. Although these war research plans were dismissed around the 1950s, new pacific applications for this class of materials came to light in the field of energy storage.

### 3. Decomposition Reactions of Li, Na, K, Mg, Ca and U Tetrahydroborates

Homoleptic tetrahydroborates have a high gravimetric hydrogen capacity. However, those compounds, stable at room temperature, can release hydrogen under thermal input. Predictions by first-principle calculations suggested that the charge transfer from  $M^+$  to  $[BH_4]_n^-$  is a crucial factor for the stability of  $M(BH_4)_n$  ( $M$  = metal). Moreover, a linear relationship between the enthalpy of  $M(BH_4)_n$  and the Pauling electronegativity ( $X_p$ ) of  $M$  was underlined [80–82]. Experimental results also demonstrated that the desorption temperatures ( $T_d$ ) of the tetrahydroborates are generally correlated with the  $X_p$  value of the metal. Gas chromatography experiments showed a decrease of the desorption temperature with the increase of  $X_p$  value of the metal, e.g.,  $T_d$ :  $(NaBH_4) \approx 550\text{ }^\circ\text{C} > (LiBH_4) \approx 470\text{ }^\circ\text{C} > (Sc(BH_4)_3) \approx 280\text{ }^\circ\text{C} > (Zr(BH_4)_4) \approx 170\text{ }^\circ\text{C} > (Zn(BH_4)_2) \approx 125\text{ }^\circ\text{C}$  with  $X_p$ :  $Na = 0.9 < Li = 1.0 < Sc = 1.3 < Zr = 1.4 < Zn = 1.6$  [82,83]. The Pauling electronegativity of the metal is also correlated with the decomposition products of tetrahydroborates. Nakamori et al. [84] reported that stable-covalent metal tetrahydroborates ( $X_p < 1.5$ ) during decomposition release hydrogen, whereas less stable-covalent tetrahydroborates ( $X_p > 1.5$ ) release a mixture of diborane and hydrogen. An important general feature of the dehydrogenation reaction of  $M(BH_4)_n$  ( $M$ : K, Na, Li, Mg, Ca, etc.) is the thermodynamically favorable formation of the  $M(B_{12}H_{12})_n$  compounds (reaction (29)). On the one hand, they are considered as intermediate compounds [85–103]. However, on the other hand, their high stability and highly negative enthalpy of formation suggest that they are final decomposition products of  $M(BH_4)_n$  [92,102–106].



Here below, the decomposition behaviors of  $KBH_4$ ,  $NaBH_4$ ,  $LiBH_4$ ,  $Mg(BH_4)_2$ ,  $Ca(BH_4)_2$ , and  $U(BH_4)_4$  are summarized. It is worth mentioning that the decomposition behavior of  $U(BH_4)_4$  is here shown because of the scarce information available about this particular borohydride, but it cannot be considered as a potential material for hydrogen storage applications.

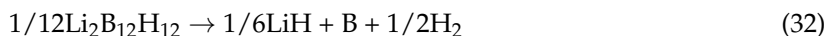
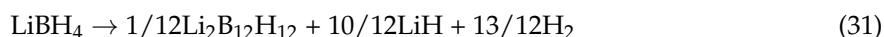
#### 3.1. $LiBH_4$

When  $LiBH_4$  is heated, a phase transition from the ordered low-temperature orthorhombic phase to the disordered high-temperature hexagonal polymorph takes place at about  $115\text{ }^\circ\text{C}$ . Increasing the temperature,  $LiBH_4$  releases a small amount of hydrogen (about 0.3 wt %) between  $100\text{ }^\circ\text{C}$  and  $200\text{ }^\circ\text{C}$ , and melts at around  $270\text{ }^\circ\text{C}$  [91,107,108]. The two main hydrogen releases occur at  $320\text{ }^\circ\text{C}$  and  $400\text{ }^\circ\text{C}$ . When heating up to  $600\text{ }^\circ\text{C}$ , the final reaction products are solid lithium hydride, solid boron, and gaseous hydrogen, as shown in reaction (30).



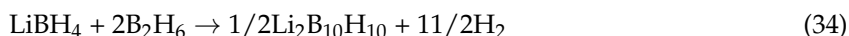
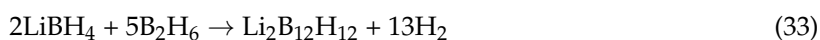
The total weight loss associated with the hydrogen release of reaction (30) is 13.8 wt % and its experimental reaction enthalpy is  $75\text{ kJ/mol } H_2$  [109]. However, reaction (30) proceeds through several different intermediate steps, as predicted via theoretical calculations and verified via

experimental evidences [85,86,89,91–93]. Computational and experimental works have reported that the decomposition reaction of  $\text{LiBH}_4$  proceeds through the formation of the intermediate  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  as indicated in reaction (31), and finally  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  decomposes to solid lithium hydride, solid boron and gaseous hydrogen according to reaction (32). This happens because the enthalpy value for reaction (31) is lower than that for reaction (30), namely 56 kJ/mol  $\text{H}_2$  and 75 kJ/mol  $\text{H}_2$ , respectively [85,86].



Caputo et al. [92] studied the decomposition reactions of  $\text{LiBH}_4$  by first-principle approach. They argued that the calculated enthalpy of formation of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  is highly negative. Hence, it is a product that hinders the reversible dehydrogenation/re-hydrogenation process of  $\text{LiBH}_4$ .

Friedrichs et al. [93] reported that together with hydrogen, small quantities of  $\text{B}_2\text{H}_6$  are released. Once formed,  $\text{B}_2\text{H}_6$  decomposes to elemental B and hydrogen or it might react with the still present  $\text{LiBH}_4$  to form  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  and possibly  $\text{Li}_2\text{B}_{10}\text{H}_{10}$  as in reactions (33) and (34), respectively.



The decomposition pathway either via the direct formation of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  (reactions (31) and (32)), or the interaction of  $\text{LiBH}_4$  and  $\text{B}_2\text{H}_6$  depends mainly on the applied gas overpressure. Under vacuum conditions the decomposition reaction can go through the formation of  $\text{B}_2\text{H}_6$ , as shown in reactions (33) and (34) [93]. However, under hydrogen or even argon overpressure the decomposition of  $\text{LiBH}_4$  may not proceed via the intermediate formation of gaseous diborane ( $\text{B}_2\text{H}_6$ ) since the gas overpressure kinetically suppresses its release [110,111]. Thus,  $\text{LiBH}_4$  decomposes through the intermediate formation of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ , as indicated in reactions (31) and (32).

### 3.2. $\text{NaBH}_4$

Upon heating,  $\text{NaBH}_4$  starts to release hydrogen at 470 °C when it is still in solid form, and continues the dehydrogenation after melting at about 515 °C through a multistep process. From dehydrogenation pressure-composition isotherms (PCI) of  $\text{NaBH}_4$  measured at 600 °C, 650 °C and 700 °C under dynamic hydrogen flow, just one plateau was observed. Thus, the decomposition of  $\text{NaBH}_4$  over 600 °C proceeds in one step and the final products are liquid sodium, solid boron, and gaseous hydrogen, with a total gravimetric  $\text{H}_2$  capacity of 10.6 wt % according to reaction (35). The experimental estimated decomposition enthalpy of reaction (35) amounts to  $108 \pm 3 \text{ kJ} \cdot \text{mol}^{-1} \text{H}_2$ , which is in agreement with the observed high stability of  $\text{NaBH}_4$  [112].



Alternatively,  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  phase has been reported experimentally as an intermediate of the decomposition of  $\text{NaBH}_4$  [94–96]. However, the high thermodynamic stability of  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  calculated by first-principle approach suggests that it should rather be considered as a product that prevents the subsequent re-hydrogenation because of its poor reactivity towards hydrogen [105]. The mechanism of formation of  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  has not been totally understood yet, but theoretical approaches suggest that  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  is a product of the reaction between boranes and unreacted  $\text{NaBH}_4$  as well as in the case of  $\text{LiBH}_4$  [92,106].



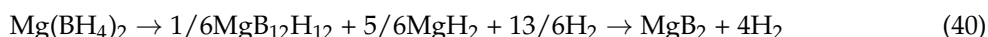
### 3.3. $\text{KBH}_4$

$\text{KBH}_4$  decomposes after melting at about 585 °C by forming potassium in liquid form, solid boron, and gaseous hydrogen, according to reaction (36). The gravimetric  $\text{H}_2$  capacity is 7.48 wt % [21,92]. The intermediate formation of  $\text{K}_2\text{B}_{12}\text{H}_{12}$  has been also predicted via first-principle calculations [97].



### 3.4. $\text{Mg}(\text{BH}_4)_2$

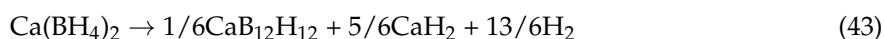
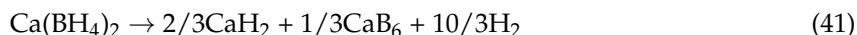
Magnesium tetrahydroborate, i.e.,  $\text{Mg}(\text{BH}_4)_2$ , has a gravimetric hydrogen storage capacity of 14.9 wt % and an enthalpy of decomposition of about 40 kJ/mol  $\text{H}_2$  [76,113–115]. Upon heating  $\text{Mg}(\text{BH}_4)_2$ , the phase transition from the hexagonal to the orthorhombic polymorph takes place at 185 °C. However, at room temperature, different polymorphs of  $\text{Mg}(\text{BH}_4)_2$  can be found, depending on the synthesis method. Experimental evidences suggest that the decomposition occurs in several steps between 250 °C and 500 °C, finally forming  $\text{MgB}_2$  and hydrogen [29,113,115–118]. The mechanism of decomposition is strongly debated and several different reaction paths can be found in the literature, as described in reactions (37)–(40) [72,98–101]. In this case, as for the  $\text{LiBH}_4$ , the final decomposition products and the presence of reaction intermediates/side products depend strongly on the applied experimental conditions.



Experimentally, it was observed that when the decomposition of  $\text{Mg}(\text{BH}_4)_2$  is carried out at temperatures above 450 °C and at a hydrogen pressure below the equilibrium pressure of  $\text{MgH}_2$ , the final products are  $\text{MgB}_2$  and  $\text{H}_2$  [98,101,108,113]. The formation of  $\text{MgB}_2$  upon decomposition is the key for the reversibility of  $\text{Mg}(\text{BH}_4)_2$ .

### 3.5. $\text{Ca}(\text{BH}_4)_2$

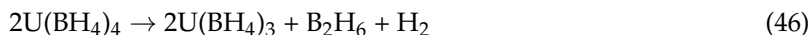
Calcium tetrahydroborate, i.e.,  $\text{Ca}(\text{BH}_4)_2$ , has a gravimetric hydrogen storage capacity of 11.6 wt %. Upon heating, it undergoes a polymorphic transition from the orthorhombic  $\alpha$ -phase to the tetragonal  $\beta$ -phase at around 170 °C. However, the polymorphs present in the samples, as well as the structural phase transitions between them, depend on the sample synthesis: for instance ball milling leads to the formation of the metastable orthorhombic  $\gamma$ -phase at room temperature [99,119–123]. Like  $\text{Mg}(\text{BH}_4)_2$ , the decomposition path of  $\text{Ca}(\text{BH}_4)_2$  is debated and several different reaction mechanisms are reported in the literature as shown in reactions (41)–(45) [102–104]:



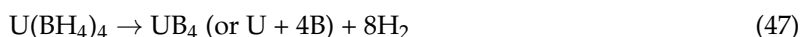
Due to extremely similar reaction enthalpies of some of the reported paths, i.e., reaction (41) = 37.04 kJ/mol  $\text{H}_2$ , reaction (43) = 31.34 – 39.2 kJ/mol  $\text{H}_2$  and reaction (44) = 31.09 kJ/mol  $\text{H}_2$ , the possibility that the decomposition of the  $\text{Ca}(\text{BH}_4)_2$  takes place following more than a single reaction path cannot be excluded [102–104].

### 3.6. $U(BH_4)_4$

At temperatures below 70 °C,  $U(BH_4)_4$  is stable for long periods. However, at about 100 °C it decomposes to form uranium (III) tetrahydroborate, diborane and hydrogen as shown in reaction (46) [124]:



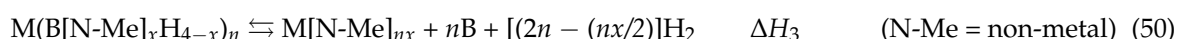
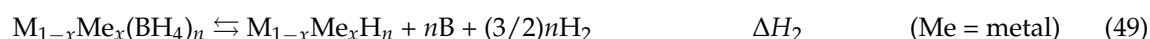
At temperatures above 150 °C, uranium (IV) tetrahydroborate rapidly decomposes to form the uranium boride, i.e.,  $UB_4$ , or elemental boron and uranium plus hydrogen, as described in reaction (47) [124]:



## 4. Tailoring the Hydrogen Storage Properties of Tetrahydroborates

Homoleptic tetrahydroborates are characterized by high decomposition temperature and extremely harsh re-hydrogenation conditions, i.e., temperatures above 400 °C and hydrogen pressures higher than 100 bar. Until the end of the 1990s, tetrahydroborates have been mostly used as laboratory reagents and have been investigated just sporadically as possible energy storage materials. However, these compounds have caught special attention owing to their promising hydrogen storage properties (light weight and high hydrogen content). Therefore, intensive research has been carried out to improve the hydrogen storage properties of tetrahydroborates, mainly  $LiBH_4$ ,  $NaBH_4$ ,  $Mg(BH_4)_2$ , and  $Ca(BH_4)_2$ . Several strategies have been applied to tailor the thermodynamic and kinetic features of the above mentioned borohydrides, aiming to reach the targets set by U.S. Department of Energy DoE [125]. The most relevant strategies are: (1) addition of catalytic additives [126–130]; (2) thermodynamic tuning via hydrides mixtures [131–135]; and, (3) nanoconfinement of tetrahydroborates and their hydride mixtures [95,132–138].

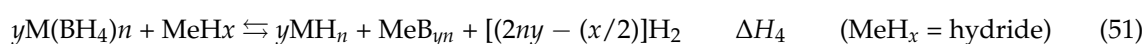
The first strategy refers to the addition of metals or metal compounds, in general transition metals, which leads to an improvement of the hydrogenation and dehydrogenation kinetic behavior by reducing the activation energy barriers and consequently accelerating the intrinsic rate limiting steps. In general, the addition of some metals and compounds also promotes a thermodynamic modification by changing the reaction pathway. This concept lays on the reduction of the thermodynamic stability and the enhancement of the kinetic behavior of tetrahydroborates ( $MBH_4$ ) by the partial substitution of M (cation substitution) [126,130], or the partial substitution of hydrogen atoms inside the  $[BH_4]^-$  anion (in general by a non-metal such as fluorine; anion substitution) [127–129]. During these processes, it is also possible to attain the formation of a new compound as a product of a favorable thermodynamic interaction between the additive and the tetrahydroborate that provides new catalytic phases. As depicted in the general reactions (48)–(50), the right selection of metal or non-metal can reduce the stability of the tetrahydroborate ( $\Delta H_2 < \Delta H_1$  and  $\Delta H_3 < \Delta H_1$ ). On the one hand, the partial cation substitution can reduce the thermodynamic stability and consequently the dehydrogenation temperature by increasing the Pauling electronegative ( $X_p$ ) (see Section 3) [130]. On the other hand, the partial anion substitution lowers the thermodynamic stability by weakening the B–H bonds. The following general reactions depict these concepts:



This strategy usually presents limited reversibility since quite stable compounds are formed.

The second strategy is the thermodynamic tuning via the use of hydrides mixtures. This concept was first explored via the formation of alloys in 1958. That year, Libowitz et al. observed that at a given temperature  $ZrNiH_3$  has a desorption pressure much higher than the one measured for

ZrH<sub>2</sub>. Thus, ZrNiH<sub>3</sub> has an enthalpy of decomposition lower than that of ZrH<sub>2</sub> [131]. Similarly, in 1967, Reilly et al. [132] reported on the possibility to change the reaction enthalpy of a hydride by mixing it with compounds with a proper stoichiometric ratio, which reversibly react with the hydride during desorption to form a stable compound. In particular, he showed that the reaction enthalpy of 3MgH<sub>2</sub> + MgCu<sub>2</sub> is lower than the one of pure MgH<sub>2</sub>. Unfortunately, the gained reduction of the reaction enthalpy is at the expense of the system's hydrogen capacity. In the last 15 years, the approach of Libowitz et al. [131] and Reilly et al. [132] has been improved by Chen et al. [133], Vajo et al. [134] and Barkhordarian et al. [135]. These researchers designed light-weight metal hydrides-based system with reduced reaction enthalpy using an appropriate combination of complex metal hydrides and metal hydrides. Such hydride mixtures are the so-called Reactive Hydride Composites (RHC). This strategy allows for the reduction of the thermodynamic stability ( $\Delta H_4 < \Delta H_1$ ) upon dehydrogenation because of the exothermic formation of a new and reversible phase, as shown in reaction (51). It offers the advantage of improved reversibility and high gravimetric storage capacity.



Despite the fact that the RHC strategy has shown good results as for example with the mixture 2LiBH<sub>4</sub> + MgH<sub>2</sub> [134,135], experimental results have proved that the predicted thermodynamic improvement is not reached due to kinetic constraints that lead to competing multi-step reactions [95,136,137].

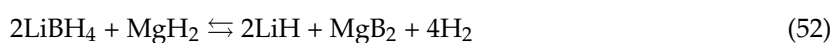
Nanoconfinement is the third presented strategy that has been recently applied to the pure tetrahydroborates, doped tetrahydroborates and the undoped and doped RHC [138–141]. It is well known that the physical and chemical properties of a material can change markedly when reducing its particle size from the micrometer range to the nanometer range. In fact, on the one hand, the enthalpy of decomposition/formation can be reduced due to the larger impact of the surface energy on the stability of the material [138] and on the other hand, the reduction of the diffusion distances and the larger specific area for the hydrogen interaction account for the kinetic enhancement [139,142].

In the following subsections some relevant results regarding the three above described strategies applied to the LiBH<sub>4</sub>, NaBH<sub>4</sub>, Mg(BH<sub>4</sub>)<sub>2</sub>, and Ca(BH<sub>4</sub>)<sub>2</sub> tetrahydroborates are summarized.

#### 4.1. LiBH<sub>4</sub>

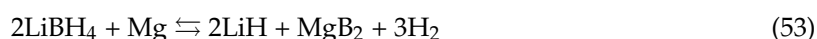
The first attempts to influence the dehydrogenation and reversibility properties of LiBH<sub>4</sub> were made by A. Züttel et al. [142] by mixing the tetrahydroborate with SiO<sub>2</sub>. They lowered the hydrogen desorption temperature by more than 70 °C. However, the formation of stable silicates upon decomposition prevented the material from being re-hydrogenated [143,144]. This effort was followed by several other researchers, who attempted to improve the hydrogen sorption properties and reversibility of LiBH<sub>4</sub> by mixing it with metal halides [126,145–150], pure metals [151–154], and carbon based additives [155,156]. Undoubtedly, the addition of these materials led to a general decrease of the LiBH<sub>4</sub> desorption temperature, but the reversibility achieved under elevated temperature and hydrogen pressure conditions (e.g., 600 °C and 100 bar H<sub>2</sub> pressure for LiBH<sub>4</sub> doped with Ni) was just partial.

The most prominent RHC system based on tetrahydroborates is 2LiBH<sub>4</sub> + MgH<sub>2</sub> [134,135,157]. According to the reaction (52), it has the reversible hydrogen storage capacity of 11.5 wt % and a theoretical reaction enthalpy of 46 kJ/mol H<sub>2</sub>, which implies a hydrogen equilibrium pressure of 1 bar at 170 °C [158].



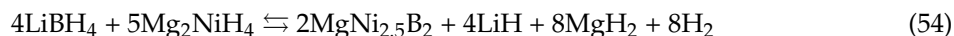
In the last decade this system has been thoroughly investigated with respect to reaction pathway, temperature and hydrogen pressure boundaries, microstructure, effect of additives on the reaction kinetics, and nanoconfinement [159–173].

For the  $2\text{LiBH}_4 + \text{MgH}_2$  system, the value of hydrogen pressure applied during the desorption process is fundamental to ensure the reversibility. In fact, when  $2\text{LiBH}_4 + \text{MgH}_2$  is heated under a hydrogen pressure lower than 1 bar,  $\text{LiBH}_4$  and  $\text{MgH}_2$  decompose individually, forming a series of compounds, which under moderate temperature and hydrogen pressures hardly react together to form again  $\text{LiBH}_4$  (i.e.,  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ ,  $\text{Li}_2\text{B}_2\text{H}_6$ ,  $\text{LiH}$ , elemental B, and Mg). However, the application of a hydrogen back pressure higher than 1 bar but lower than 5 bar ensures the possibility to reversibly release under moderate temperature the hydrogen contained in the system. Under dynamic temperature conditions, the decomposition reaction takes place in two distinguished steps. At first, the decomposition of  $\text{MgH}_2$  into Mg and  $\text{H}_2$  occurs, and then, after a long incubation period, Mg reacts together with  $\text{LiBH}_4$  to form  $\text{MgB}_2$ ,  $\text{LiH}$  and  $\text{H}_2$  as shown in reaction (53). Differently from the desorption reaction, the hydrogenation process takes place in a single step [136].



Despite the favorable calculated enthalpy of reaction and the high gravimetric hydrogen capacity, the sluggish kinetics is the primary issue of this system. In the last decade, several studies on the effect of transition metal based additives were carried out. The nucleation of  $\text{MgB}_2$  is the key issue for a fast dehydrogenation kinetic behavior and it is enhanced by the presence of transition metal borides that act as nucleation center for the  $\text{MgB}_2$  nuclei [159]. Although the reaction times are much different with and without additives, analyses of the reaction kinetics indicate that similar processes limit the sorption reactions for all the composites, independently of the additive and the initial preparation state. The absorption and desorption reactions in the RHC are characterized by significant mass transport through the composite, and therefore, the length scales of the phase separation play a significant role in the reaction kinetics.

Another RHC system that presents interesting hydrogen storage properties is the combination of  $\text{LiBH}_4$  and  $\text{Mg}_2\text{NiH}_4$ , according to reaction (54). This hydride system exhibits a low reaction enthalpy of 15.4 kJ/mol  $\text{H}_2$  and an entropy value of 62.2 J/K mol  $\text{H}_2$ . Moreover, it starts to release hydrogen at 250 °C [174].



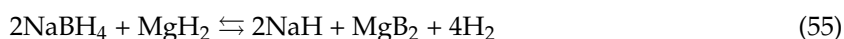
Despite the fact that this system does not display a high hydrogen capacity, i.e., 2.5 wt %, it represents another example of reversible RHC systems.

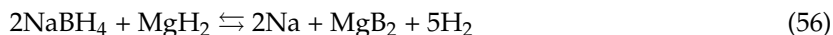
#### 4.2. $\text{NaBH}_4$

The effect of the doping on the reversibility of  $\text{NaBH}_4$  was studied mostly by Mao et al. [175] and Humphries et al. [176]. They observed a sensible enhancement of the hydrogen desorption properties of  $\text{NaBH}_4$  when Ti-based (i.e., Ti,  $\text{TiH}_2$ , and  $\text{TiF}_3$ ) and Ni-based additives (i.e., nano-Ni,  $\text{Ni}_3\text{B}$ ,  $\text{NiCl}_2$ , and  $\text{NiF}_2$ ) were used. However, partial reversibility was achieved only in the case of Ti-based additives. In fact, when using  $\text{TiF}_3$ , a hydrogen content of 4.0 wt % was stored back in the decomposed  $\text{NaBH}_4$  after hydrogenation at 55 bar and 500 °C.

In order to improve the hydrogen storage properties of  $\text{NaBH}_4$ , nanocomposites of  $\text{NaBH}_4$ -C with a matrix of 2 to 3 nm pore size diameter were synthesized. This allowed the lowering of the dehydrogenation temperature of  $\text{NaBH}_4$  down to 250 °C. However, the re-hydrogenation under 60 bar and 325 °C was not completed due to the loss of Na upon dehydrogenation [96].

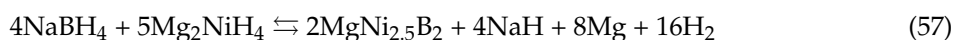
As in the case of the mixture  $2\text{LiBH}_4 + \text{MgH}_2$ , the RHC based on  $2\text{NaBH}_4 + \text{MgH}_2$  is reversible because of the formation of  $\text{MgB}_2$  upon desorption. The dehydrogenation reactions of the  $2\text{NaBH}_4 + \text{MgH}_2$  can proceed either as reaction (55) with 7.8 wt %  $\text{H}_2$  or reaction (56) with 9.8 wt %  $\text{H}_2$ , depending on the conditions [177–179].





However, the dehydrogenation of this system also goes on in two steps under 1 bar of inert gas, i.e., first the dehydrogenation of  $\text{MgH}_2$  and then the subsequent formation of  $\text{MgB}_2$  [178,180]. Furthermore, the formation of stable side products such as  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  has been also suggested [180]. Under vacuum, the pathway is different and it involves the formation of free Mg and finally free B [181].

As well as the  $\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$  mixture, the stoichiometric ratio  $4\text{NaBH}_4 + 5\text{Mg}_2\text{NiH}_4$  also leads to the formation of  $\text{MgNi}_{2.5}\text{B}_2$ , lowering the enthalpy of the hydride system to 76 kJ/mol  $\text{H}_2$  in respect to the one of pure  $\text{NaBH}_4$  (108 kJ·mol<sup>−1</sup>  $\text{H}_2$ ), as shown in reaction (57) [112,182]. Consequently, the dehydrogenation temperature is reduced to 360 °C. However, the hydrogen capacity of the system is still low, i.e., 4.5 wt %.



#### 4.3. $\text{Mg}(\text{BH}_4)_2$

The effect of additives on the reversibility of  $\text{Mg}(\text{BH}_4)_2$  has been an object of intensive investigation [101,183–188]. The result of the doping seems to be a sensible acceleration of hydrogenation and dehydrogenation processes. However, in the literature, just a few hydrogenation-dehydrogenation cycles are reported and the observed enhancement of the reaction kinetics, in particular for the desorption process, is usually connected with the chemical reaction between the hydride and the additive. Recently, Zavarotynska et al. reported on the partial reversibility of  $\gamma\text{-Mg}(\text{BH}_4)_2$  in presence of Co-based additives ( $\text{Co}_{\text{add}}$ ) [187,188]. They investigated the first three absorption-desorption cycles of  $\gamma\text{-Mg}(\text{BH}_4)_2 + \text{Co}_{\text{add}}$  at 285 °C and 3 bar  $\text{H}_2$  pressure. The first desorption yielded 4 wt % of  $\text{H}_2$ , and the re-absorption at the same temperature but at the pressure of 120 bar  $\text{H}_2$  resulted in the uptake of about 2 wt %  $\text{H}_2$ . Upon re-absorption,  $\gamma\text{-Mg}(\text{BH}_4)_2$  was not formed back, but instead crystalline  $\beta\text{-Mg}(\text{BH}_4)_2$  was synthesized. With further cycling, the reversible hydrogen capacity of the samples decreased with an increase in the amount of nano-crystalline MgO and unidentified boron–hydrogen compounds.

Although the addition of selected additives to the tetrahydroborates partially helps to improve the hydrogen absorption and desorption properties, the use of this class of materials as hydrogen storage media is hampered by unfavorable thermal stability.

#### 4.4. $\text{Ca}(\text{BH}_4)_2$

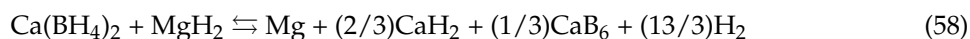
As previously mentioned, for  $\text{Ca}(\text{BH}_4)_2$  several decomposition paths (often overlapping) might be observed (Section 3.5), depending on temperature and hydrogen pressure at which the process is carried out [100–102,189]. The reversibility is linked to the final decomposition products. The formation of  $\text{Ca}(\text{BH}_4)_2$  was shown to be partially reversible when the pristine material was doped with Ti and Nb-based additives. Kim et al. [190,191] observed that after desorption at 420 °C in static vacuum,  $\text{Ca}(\text{BH}_4)_2$  can be formed back with a yield of roughly 50% (at 350 °C and 90 bar  $\text{H}_2$ ), if the starting material is milled together with  $\text{TiCl}_3$  and  $\text{NbF}_5$ . From these works, it is possible to conclude that the key to the reversibility of  $\text{Ca}(\text{BH}_4)_2$  is the formation of  $\text{CaB}_6$ . It is known that when using selected additives,  $\text{Ca}(\text{BH}_4)_2$  can be synthesized starting from  $\text{CaH}_2$  and  $\text{CaB}_6$  [190,192–194]. In fact, Rönnebro et al. successfully synthesized  $\text{Ca}(\text{BH}_4)_2$  with the yield of roughly 60% heating a mixture of  $\text{CaH}_2$  and  $\text{CaB}_6$  doped with  $\text{TiCl}_3$  up to 440 °C at a hydrogen pressure of 700 bar [194]. A similar yield of formed  $\text{Ca}(\text{BH}_4)_2$  was obtained by Rongeat et al. [193] via reactive ball milling and following heat treatment at 350 °C under 90 bar of hydrogen pressure of a mixture of  $\text{CaH}_2$  and  $\text{CaB}_6$  with the addition of  $\text{TiCl}_3$  or  $\text{TiF}_3$ .

Recently, Bonatto Minella et al. [195], based on the work of Bösenberg et al. [159], proposed an interesting approach to explain the effect of the TM-fluorides on the reversibility of the  $\text{CaB}_6/\text{CaH}_2\text{--Ca}(\text{BH}_4)_2$  system. The formation of transition-metal boride nanoparticles during milling, and hydrogen desorption of the TM-fluorides doped  $\text{Ca}(\text{BH}_4)_2$  are proposed to support the heterogeneous

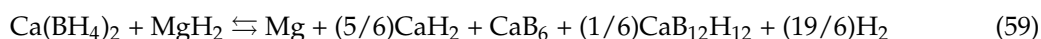


nucleation of  $\text{CaB}_6$ , maximizing its formation over the formation of irreversible elemental boron and  $\text{CaB}_{12}\text{H}_{12}$ . In the case of material doped with  $\text{NbF}_5$  and  $\text{TiF}_4$ , the  $\{111\}\text{CaB}_6/\{1011\}\text{NbB}_2$ ,  $\{111\}\text{CaB}_6/\{1010\}\text{NbB}_2$ , as well as  $\{111\}\text{CaB}_6/\{1011\}\text{TiB}_2$  plane pairs have the potential to be the matching planes because the  $d$ -value mismatch is well below the  $d$ -critical mismatch value (6%) [196,197]. This mechanism is similar to that observed for  $2\text{LiBH}_4 + \text{MgH}_2$ . Transition metal borides formed by the reaction of the transition metal based additives with the tetrahydroborates act as heterogeneous nucleation sites for  $\text{MgB}_2$ , thus improving desorption and absorption reaction kinetics [159].

Despite the fact that the TM-boride species assist the formation of  $\text{CaB}_6$ , the reversibility of the Ca-RHC system, i.e.,  $\text{Ca}(\text{BH}_4)_2 + \text{MgH}_2$  as shown in reaction (58), is not complete [137,198–200].



Instead, every time that the material is cycled, the formation of stable phases such as  $\text{CaB}_{12}\text{H}_{12}$  and elemental B takes place as indicated in reaction (59) and (42), respectively. Consequently, a continuous reduction of the system hydrogen capacity takes place upon cycling.



Based on the previous works on  $4\text{LiBH}_4 + 5\text{Mg}_2\text{NiH}_4$  [174] and  $4\text{NaBH}_4 + 5\text{Mg}_2\text{NiH}_4$  [184], Bergemann et al. [201] proposed as an alternative the combination of  $\text{Ca}(\text{BH}_4)_2$  with  $\text{Mg}_2\text{NiH}_4$ . In this system, upon dehydrogenation, the formation of  $\text{MgNi}_{2.5}\text{B}_2$  as the only B-containing phase is observed according to reaction (60). There was no evidence of the presence of irreversible  $\text{CaB}_{12}\text{H}_{12}$  and B. However, upon re-hydrogenation  $\text{Ca}(\text{BH}_4)_2$  was only partially formed. This limited reversibility was attributed to thermodynamic and kinetic constraints.



## 5. Summary and Future Research Directions

In this review, a detailed account on selected aspect of the most relevant tetrahydroborates and tetrahydroborate-based systems investigated in the last decades as potential hydrogen storage candidates was reported. As a matter of fact, these materials used alone or as a part of RHC systems have some limitations, which make their use for practical applications challenging. Owing to their high gravimetric hydrogen capacity, tetrahydroborates are extremely appealing hydrogen storage materials. However, the contained hydrogen is not easily accessible. Under thermal input, tetrahydroborates such as  $\text{LiBH}_4$ ,  $\text{NaBH}_4$ ,  $\text{K}(\text{BH}_4)$ ,  $\text{Mg}(\text{BH}_4)_2$ , and  $\text{Ca}(\text{BH}_4)_2$  decompose at temperatures higher than  $300^\circ\text{C}$ , and their decomposition products are partially reversible only under extreme temperature and hydrogen pressure conditions. Additives such as transition metals, transition metal halides or oxides, sensibly influence the decomposition reaction of these materials, often lowering the starting decomposition temperature by several tenths of degrees. However, the reversibility of the material still remains an issue since stable phases are formed upon decomposition. The hitherto most promising approach to effectively store hydrogen in tetrahydroborates is through the use of the RHC strategy. When compared to the pristine materials, this method enables the achievement of full reversibility under milder temperatures and hydrogen pressure conditions, e.g.,  $350\text{--}400^\circ\text{C}$  and 3 bar–50 bar for  $2\text{LiBH}_4 + \text{MgH}_2$ . Despite the fact that these conditions, mainly temperature, are not even near to those required for on board practical application (desired temperature  $\approx 90^\circ\text{C}$ ), there has been an attempt to develop a demonstration hydrogen storage tank based on  $2\text{LiBH}_4 + \text{MgH}_2$  [202]. This tank contained 250 g of material. It has been found that during operation, the thermal management becomes an important issue, and the material undergoes a long-range phase separation, which negatively affects the kinetic behavior and the hydrogen capacity of the system. To the best of our knowledge, this was the first tank design based on borohydrides and it has to be considered as a starting point in the

development of tetrahydroborates based systems for hydrogen storage. Nowadays, the research is directed to find better systems capable to work near to the targeted temperature condition of about 90 °C and at the same time characterized by a hydrogen storage capacity of about 10 wt %. Besides, the cost of the material is not a minor issue when one wants to employ such materials in large hydrogen storage tanks.

In spite of several efforts to find the proper tetrahydroborate-based systems, the correct additive and suitable material preparation procedure, it has not yet been possible to achieve complete hydrogen desorption/absorption at the theoretically expected temperature and hydrogen pressure conditions. Moreover, the hydrogenation-dehydrogenation cycling stability is still a key issue to be addressed. Although tetrahydroborates are known for more than a century, the major achievements towards their utilization have been obtained in the last 20 years. Based on this perspective, the hydrogen storage properties of tetrahydroborates can be further improved by different strategies that are broadly used nowadays, such as the RHC approach, the use of selected additives, and/or nanoengineering. Thus, in the near future tetrahydroborates will hopefully fulfill the conditions for a practical application.

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